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Abstract

The policy-relevant background (PRB) ozone is defined by the US Environmental Protection Agency (EPA) as the surface ozone concentration that would be present over the US in the absence of North American anthropogenic emissions. It is intended to provide a baseline for risk and exposure assessments used in setting the National Ambient Air Quality Standard (NAAQS). We present here three-year statistics (2006-2008) of PRB ozone over the US calculated using the GEOS-Chem global 3-D model of atmospheric composition with 1/2° × 2/3° horizontal resolution over North America and adjacent oceans (2° × 2.5° for the rest of the world). We also provide estimates of the US background (no anthropogenic US emissions) and natural background (no anthropogenic emissions worldwide and preindustrial methane). PRB is particularly high in the intermountain West due to high elevation, arid terrain, and large-scale subsidence. We present for this region a detailed model evaluation showing that the model is successful in reproducing ozone exceedances up to 70 ppbv. However, the model cannot reproduce PRB-relevant exceptional events associated with wildfires or stratospheric intrusions. The mean PRB estimates for spring-summer are 27 ± 8 ppbv at low-altitude sites and 40 ± 7 ppbv at high-altitude sites. These include a mean enhancement from intercontinental pollution and anthropogenic methane of 9 ppbv at low-altitude sites and 13 ppbv at high-altitude sites. The PRB is higher than average when ozone exceeds 60 ppbv, particularly in the intermountain West. The annual 4th-highest PRB values in the intermountain West are typically 50-60 ppbv, as compared to 35-45 ppbv in the East or on the West Coast. Our PRB estimates are on average 4 ppbv higher than in previous GEOS-Chem studies and this may reflect higher lightning, increasing Asian emissions, and improved model resolution.

Keywords: Ozone; background ozone; policy relevant background; air quality standard

1. Introduction

The US Environmental Protection Agency (US EPA, 2006) defines the policy-relevant-background (PRB) for ozone air quality as the surface ozone concentration that would be present in the US in the absence of anthropogenic emissions from North America (defined as the ensemble of the US, Canada, and Mexico). The PRB is used in the setting of the National Ambient Air Quality Standard (NAAQS) to estimate the maximum ozone reduction that could be achieved through North American emission controls. It provides a baseline for risk and exposure assessments. The present US NAAQS is 75 ppbv (annual 4th-highest daily maximum 8-h average concentration), but the EPA is considering decreasing it to a value in the 60-70 ppbv range. As the standard becomes more stringent and approaches the PRB, accurate specification of the PRB becomes increasingly important

Ozone is produced in the troposphere by photochemical oxidation of CO and volatile organic compounds (VOCs) in the presence of nitrogen oxides ($NO_x \equiv NO + NO_2$). It is also transported to the troposphere from the stratosphere. The NO_x, CO, and VOC

precursors of ozone have major anthropogenic sources from fuel combustion as well as natural sources including lightning, wildfires, and the biosphere. Ozone has a lifetime of only a few days in the continental boundary layer but weeks in the free troposphere (Y. Wang et al., 1998; Fiore et al., 2002). Ozonesonde, aircraft, and satellite observations show typical ozone concentrations of 50-70 ppbv in the free troposphere over North America (Thompson et al., 2007; L. Zhang et al., 2010), with frequent occurrence over 80 ppbv in plumes from intercontinental pollution, fires, and stratospheric intrusions (Heald et al., 2003; Nowak et al., 2004; Bertschi and Jaffe, 2005; Liang et al., 2007; Thompson et al., 2007; Oltmans et al., 2010). Subsidence of this high-ozone air to the surface could result in PRB values approaching or exceeding the NAAQS (Jaffe, 2011). However, ozone decreases during entrainment into the boundary layer because of dilution, deposition, and chemical loss (Fiore et al., 2002; Hudman et al., 2004; L. Zhang et al., 2009; Cooper et al., 2011).

A region of particular interest from a PRB perspective is the intermountain West, extending between the Sierra Nevada/Cascades Mountains to the west and the Rocky Mountains to the east. This region features elevated plateaus and mountains with surface elevations typically in excess of 1.5 km, arid terrain, and large-scale subsidence. As a result, background ozone there is higher than in the eastern US (Lefohn et al., 2001; Fiore et al., 2002; Jaffe, 2011). Exceptionally high ozone events have been observed in association with stratospheric intrusions (Langford et al., 2009). Positive correlations have been observed between ozone and regional wildfires (Jaffe et al., 2008; Jaffe, 2011). There is evidence that ozone inflow from the Pacific to the western US has been increasing over the past decades (Lin et al., 2000; Jaffe and Ray, 2007; Parrish et al., 2009; Cooper et al., 2010). This could reflect increasing Siberian wildfires (Jaffe et al., 2004) and Asian pollution (L. Zhang et al., 2008; Cooper et al., 2010).

The PRB ozone is not an observable quantity, if only because of the contribution of North American anthropogenic sources to the northern mid-latitudes ozone background. It needs to be calculated with a global model of atmospheric composition that is evaluated with observations at remote sites where the PRB drives much of the variability. Fiore et al. (2003) previously used the GEOS-Chem CTM with $2° \times 2.5°$ global horizontal resolution to estimate PRB ozone over the US. H. Wang et al. (2009) updated those estimates by using a $1° \times 1°$ nested continental-scale version of GEOS-Chem, and also estimated the US background ozone (defined by zeroing anthropogenic US emissions). Here we present a further update of PRB, US background, and natural background ozone estimates with a 3-year (2006-2008) GEOS-Chem simulation at $1/2° \times 2/3°$ resolution featuring a number of improvements over previous versions. Our motivation for this work is to assist the EPA in its revision of the ozone NAAQS, scheduled to be released in 2014. We include a detailed model evaluation in the intermountain West where elevated PRB is of particular relevance to the NAAQS.

2. Model description

We use the GEOS-Chem 3-D global model of atmospheric composition (v8-02-03; http://acmg.seas.harvard.edu/geos/). The model is driven by GEOS-5 assimilated

meteorological fields from the NASA Global Modeling and Assimilation Office (GMAO). Meteorological fields in the GEOS-5 data have a temporal resolution of 6 hours (3 hours for surface variables and mixing depths) and a horizontal resolution of 1/2° latitude by 2/3° longitude. GEOS-Chem includes a detailed simulation of tropospheric ozone-NO_x-VOC-aerosol chemistry. The ozone simulation over the US and adjacent oceans has been previously evaluated with measurements from surface sites (Fiore et al., 2002, 2003; Goldstein et al., 2004; H. Wang et al., 2009), aircraft (Hudman et al., 2007; L. Zhang et al., 2008; Walker et al., 2010), ozonesondes (Li et al., 2002, 2005), and satellites (Parrington et al., 2008; L. Zhang et al., 2010). L. Zhang et al. (2010) found in particular that the GEOS-Chem simulation for 2006 is unbiased in the middle troposphere at northern mid-latitudes compared with ozonesondes and satellite measurements.

We use a nested version of GEOS-Chem (Y.X. Wang et al., 2004; Chen et al., 2009; Y.X. Wang et al., 2011) with the native 1/2° × 2/3° horizontal resolution over North America and adjacent oceans (140°-40°W, 10°-70°N), and 2° × 2.5° horizontal resolution for the rest of the world. We first conduct the global GEOS-Chem simulation at 2° × 2.5° resolution, and then use the output archived at 3-hour temporal resolution as dynamic boundary conditions for the nested model.

Global anthropogenic emissions are from the Emission Database for Global Atmospheric Research (EDGAR) inventory (Olivier and Berdowski, 2001) for 2000, superseded by regional emission inventories from the EPA 2005 National Emission Inventory (NEI-05) for the US, Q. Zhang et al. (2009) for Asia in 2006, the European Monitoring and Evaluation Program (EMEP) for Europe (Vestreng and Klein, 2002), the Canada Criteria Air Contaminants (CAC) emission inventory for Canada (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), and the Big Bend Regional Aerosol and Visibility Observational (BRAVO) emission inventory for Mexico (Kuhns et al., 2005). The EMEP, CAC, and BRAVO emissions are scaled on the basis of energy statistics to 2006 as described by van Donkelaar et al. (2008). We doubled the Japanese and Korean NO_x anthropogenic emissions from Q. Zhang et al. (2009) as constrained by OMI tropospheric NO_2 column measurements (L. Zhang et al. 2008). Anthropogenic NO_x emissions from fertilizer application are from Yienger and Levy (1995).

Natural sources of ozone include open fires, lightning, the biosphere, and transport from the stratosphere. We use monthly biomass burning emissions from the Global Fire Emission Database version 2 (GFED-v2) (van der Werf et al., 2006). Lightning NO_x emissions are linked to deep convection following the parameterization of Price and Rind (1992) with vertical profiles from Pickering et al. (1998). The global spatial distribution of lightning flashes is rescaled to match the 10-year climatology of OTD/LIS satellite observations (Sauvage et al., 2007) with higher NO_x yield per flash at northern mid-latitudes than in the tropics (Hudman et al., 2007). The global lightning source is imposed to be 6 Tg N a^{-1} (Martin et al., 2007). Soil NO_x emissions are computed using a modified version of the Yienger and Levy (1995) algorithm with canopy reduction factors as described in Y. Wang et al. (1998). Stratospheric ozone is simulated with a linearized

ozone (Linoz) parameterization (McLinden et al., 2000) that provides a mechanistic representation of stratospheric influences on tropospheric ozone.

We conducted three-year GEOS-Chem simulations for 2006-2008. The standard simulation includes all sources and is used for evaluation with observations. We also conducted simulations with: (1) zero North American anthropogenic emissions (North American background or PRB) for 2006-2008, (2) zero US anthropogenic emissions (US background) for 2006, and (3) zero anthropogenic emissions worldwide and methane set to its 700 ppbv pre-industrial value (natural background) for 2006. All ozone concentrations presented in this paper are daily 8-h average maxima (daily 8-h max), the metric used for the US NAAQS. We find that the US background is on average 1-3 ppbv higher than the North American background, reflecting anthropogenic sources in Canada and Mexico, with little variability except in border regions. Our results for the US background are similar to those reported in the focused GEOS-Chem analysis of H. Wang et al. (2009) and hence we do not discuss them further.

3. Evaluation with observations in the intermountain West

We evaluated our GEOS-Chem simulation with the nationwide ensemble of surface ozone observations from the Clean Air Status and Trends Network (CASTNet; http://www.epa.gov/castnet), which monitors air quality in rural areas. The CASTNet sites are shown in Figure 1. Comparison results are generally consistent with the previous GEOS-Chem evaluations presented by Fiore et al. (2003) and H. Wang et al. (2009); time series for individual sites and summary statistics for each region are given in the Supplementary Materials. We focus here on the 12 sites in the intermountain west US, identified in Figure 1 and listed in Table 1, for the year 2006. Interannual variability for seasonal mean concentrations at individual sites is weak during 2006-2008 in both model and observations, generally less than 2 ppbv. However, interannual variation in the number of exceedance days for thresholds of 65-75 ppbv is larger as discussed in Jaffe (2011).

Figure 2 shows the time series of observed vs. simulated daily 8-h max ozone concentrations in spring-summer 2006 at four representative sites in the intermountain West, and Figure 3 shows scatterplots for the ensemble of sites. Spring-summer is when concentrations are highest. Also shown in the figures are the North American background (PRB) and natural background values. Mean values and correlation coefficients for the simulated vs. observed ozone time series at all 12 sites are summarized in Table 1. We find that seasonal mean ozone concentrations in the model are generally within ±2 ppbv of the observations in Table 1. The correlation coefficients between model and observations are only 0.2-0.5 for the individual sites, which may reflect the small dynamic range of variability in the observations. The correlation coefficient is 0.6 in spring and 0.3 in summer for the ensemble of sites in Figure 3.

The North American background (PRB) averages 39-44 ppbv (spring) and 35-45 ppbv (summer) for the ensemble of sites in the intermountain West and drives most of the day-to-day variability. The North American anthropogenic enhancement (difference between

standard and PRB simulations) averages only 10-22 ppbv depending on the site. As shown in Figure 3, PRB increases with increasing ozone concentration in the intermountain West, whereas for surface sites in the East there is little correlation of PRB with ozone (see Supplementary Materials). The natural background is on average 25-28 ppbv (spring) and 25-33 ppbv (summer) and is strongly correlated with the PRB. The model difference between the PRB and natural ozone reflects intercontinental pollution influences plus anthropogenic methane. It averages 13-16 ppbv in spring and 11-13 ppbv in summer. Intercontinental pollution influence on ozone is larger in spring because of stronger winds and slower chemical loss (Jacob et al., 1999). Annual 4th-highest ozone values at the intermountain West sites are 51-59 ppbv for PRB and 34-45 ppbv for the natural background.

It is of particular interest to evaluate the ability of the model to reproduce the frequencies of exceedance of proposed air quality standards. Figure 4 shows the simulated vs. observed number of days at individual sites when daily 8-h max ozone concentrations exceed thresholds of 60, 65, and 70 ppbv in spring and summer 2006. The model captures most of the ozone exceedances except for the 65 and 70 ppbv thresholds in spring and for the Mesa Verde site in summer. There is observational evidence that stratospheric intrusions cause high-ozone events in the intermountain West in spring (Langford et al., 2009) and these may not be properly represented in the model. The Mesa Verde model overestimate may reflect excessive summer lightning NO_x emissions over Mexico and the US Southwest.

When the ensemble of sites is considered as in Figure 3, we find that the model can provide an unbiased ozone simulation up to about 75 ppbv but fails to reproduce exceptional events of higher concentrations. Such events are illustrated in Figure 2 for Pinedale (80 ppbv) and Rocky Mountain NP (91 ppbv). This may reflect a general difficulty in Eulerian models to preserve the structure of plumes of dimensions comparable to the grid resolution (Rastigeyev et al., 2010).

4. Distribution of background ozone and contribution to pollution episodes.

Figure 5 shows the simulated and observed frequency distributions of ozone for the ensemble of CASTNet sites in the US in March-August 2006, separately for low-altitude (< 1.5 km) and high-altitude sites. Also shown are the model frequency distributions for North American (PRB) and natural ozone backgrounds. The model is unbiased in its simulation of the overall distribution. The PRB averages 27 ± 8 ppbv at the low-altitude sites and 40 ± 7 ppbv at the high-altitude sites. The natural background averages 18 ± 6 ppbv at the low-altitude sites and 27 ± 6 ppbv at the high-altitude sites. The difference between PRB and natural background reflects intercontinental pollution influence including anthropogenic methane; it averages 9 ppbv at the low-altitude sites and 13 ppbv at the high-altitude sites. The mean 2006 value of the annual 4th-highest daily 8-h max ozone is 54 ppbv for PRB and 39 ppbv for the natural background at the ensemble of high-altitude sites, compared with 42 ppbv for PRB and 29 ppbv for the natural background at the low-altitude sites.

Our general PRB statistics for the US can be compared to the previous GEOS-Chem studies of Fiore et al. (2003) and H. Wang et al. (2009). H. Wang et al. (2009) found a mean PRB of 26 ± 8 ppbv for summer 2001, whereas we find 30 ± 10 ppbv for summers 2006-2008. Fiore et al. (2003) reported a typical PRB range of 15-35 ppbv for March-October 2001 using a slightly different metric (mean afternoon concentrations). Our results are overall about 4 ppbv higher than these previous estimates. A contributing factor is our higher lightning NO_x source, 6 Tg a^{-1} as compared to 4.5 Tg N a^{-1} in H. Wang et al. (2009). Another factor is the 2001-2006 increase in Asian anthropogenic NO_x emissions, which we previously estimated to have increased PRB ozone by up to 3 ppbv in the West in spring (L. Zhang et al., 2008). We also find some dependence on the model resolution, as our outer nest with $2° \times 2.5°$ horizontal resolution yields mean PRB values that are 1-2 ppbv lower than the nested simulation. Our results are consistent with those of Parrington et al. (2009), who found a 5 ppbv increase in background ozone in the western US compared to Fiore et al. (2002) after assimilation of TES satellite ozone data into the GEOS-Chem model.

Figure 6 shows the spatial distribution of the seasonal mean PRB ozone concentrations for spring and summer 2006. The PRB is highest in the intermountain West because of the combination of high elevation, deep boundary layer mixing, large-scale subsidence, slow ozone deposition to the arid terrain, and slow ozone chemical loss due to dry conditions (Fiore et al., 2002). The PRB ozone generally decreases from spring to summer, reflecting faster chemical ozone loss; this seasonal decrease is particularly pronounced in the Northeast and on the West Coast. An increase in PRB from spring to summer is found in the Southwest due to summer lightning. The maximum PRB value over New Mexico in summer reflects intense lightning and deep boundary layer mixing.

Also shown in Figure 6 is the mean PRB ozone on the days when simulated daily 8-h max ozone exceeds 60 ppbv. We find that the mean PRB on these high-ozone days is higher than the seasonal mean almost everywhere. The difference is particularly pronounced in the West, where the PRB is on average 7 ppbv higher than the seasonal mean for both spring and summer. It is also large in the Great Lakes region in spring where high ozone values are associated with model lightning. Fiore et al. (2002) previously found PRB values to be maximum for ozone concentrations in the 50-70 ppbv range, and this is consistent with our result. If the NAAQS is lowered in the 60-70 ppbv range, areas of the intermountain West will have little or no ability to reach compliance through North American regulatory controls.

Finally, we show in Figure 7 the simulated annual 4^{th}-highest North American background (PRB) ozone in surface air averaged over 2006-2008, representing the lowest air quality standard that can be achieved by North American emission controls. Values are typically 35-45 ppbv in the East and on the West Coast but 50-60 ppbv in the intermountain West, with a maximum of 64 ppbv over New Mexico and a secondary maximum of 59 ppbv over Idaho due to large wildfires in 2007. A recent study with the CMAQ regional model found much larger contributions from wildfires on surface ozone in the western US (Mueller and Mallard, 2011). Aircraft observations of California fire

plumes indicate however no significant ozone enhancements unless mixed with urban pollution (Singh et al., 2010).

5. Conclusions

We have used the GEOS-Chem global 3-D model of atmospheric composition with 1/2° × 2/3° nested horizontal resolution over North America to provide updated estimates of the PRB ozone for the US in 2006-2008. Our work is intended to assist the US EPA in its current risk and exposure assessments as part of the NAAQS-setting process.

We evaluated the GEOS-Chem simulation with the ensemble of ozone observations from CASTNet sites across the US. Comparisons show in general similar results to previous GEOS-Chem PRB studies (Fiore et al., 2003; H. Wang et al., 2009) and are documented in the Supplementary Materials. We focused our attention on the intermountain West, where the PRB is particularly high and may interfere with the achievability of ozone air quality standards. We showed that the model gives an unbiased representation of ozone in that region and that the PRB drives most of the ozone variability. The model captures the frequency of high-ozone events up to about 70 ppbv but fails to reproduce events of exceptionally high ozone that may be due to stratospheric or wildfire influences. We expect following Rastigeyev et al. (2009) that Eulerian models in general would have difficulty in capturing exceptional events.

We obtained mean PRB values for the US in spring-summer of 27 ± 8 ppbv at low-altitude sites (< 1.5 km) and 40 ± 7 ppbv at high-altitude sites. These values are 9-13 ppbv higher than the natural background due to intercontinental pollution including anthropogenic methane. Our PRB estimates are on average 4 ppbv higher than in previous GEOS-Chem studies (Fiore et al., 2003; H. Wang et al., 2009) and we attribute this to a combination of increasing Asian emissions, higher model lightning, and higher model resolution. We find that the PRB generally decreases from spring to summer except in regions strongly affected by summer lightning. We also find that the PRB is higher than average when ozone exceeds 60 ppbv, particularly in the intermountain West. The annual 4^{th}-highest PRB value in the model (representing the minimum standard achievable through suppression of North American anthropogenic emissions) is typically in the 35-45 ppbv range over the East and the West Coast but 50-60 ppbv in the intermountain West. Such high PRB values in the intermountain West compared to the proposed revisions of the ozone NAAQS (60-70 ppbv) suggest that special consideration of that region may be needed in the NAAQS-setting process.

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References

Bertschi, I. T., Jaffe, D. A., 2005. Long-range transport of ozone, carbon monoxide, and aerosols to the NE Pacific troposphere during the summer of 2003: Observations of

smoke plumes from Asian boreal fires. Journal of Geophysical Research 110, D05303, doi:10.1029/2004JD005135.

Chen, D., Wang, Y.X., McElroy, M.B., He, K., Yantosca, R.M., Le Sager, P., 2009. Regional CO pollution in China simulated by the high-resolution nested-grid GEOS-Chem model, Atmospheric Chemistry and Physics 11, 3825-3839.

Cooper, O. R., Parrish, D. D., Stohl, A., et al., 2010. Increasing springtime ozone mixing ratios in the free troposphere over western North America. Nature 463, 7279, 344–348.

Cooper, O. R., Oltmans, S. J., Johnson, B. J., et al., 2011. Measurement of western U.S. baseline ozone from the surface to the tropopause and assessment of downwind impact regions. Journal of Geophysical Research, manuscript submitted.

Fiore, A.M., Jacob, D.J., Bey, I., Yantosca, R.M., Field, B.D., Fusco, A.C., 2002, Background ozone over the United States in summer: origin, trend, and contribution to pollution episodes. Journal of Geophysical Research 107 (D15), doi:10.1029/2001JD000982.

Fiore, A.M., Jacob, D.J., Liu, H., Yantosca, R.M., Fairlie, T.D., Li, Q.B., 2003. Variability in surface ozone background over the United States: Implications for air quality policy, Journal of Geophysical Research 108, 4787, doi:10.1029/2003JD003855.

Goldstein, A.H., Millet, D.B., McKay, M., Jaegle, L., Cooper, O., Hudman, R., Jacob, D.J., Oltmans, S., Clarke, A., 2004. Impact of Asian emissions on observations at Trinidad Head, California during ITCT 2K2. Journal of Geophysical Research 109 (D23), D23S17.

Heald, C.L., Jacob, D.J., Fiore, A.M., et al., 2003. Asian outflow and trans-Pacific transport of carbon monoxide and ozone pollution: An integrated satellite, aircraft, and model perspective. Journal of Geophysical Research 108 (D24), 4804, doi:10.1029/2003JD003507.

Hudman, R.C., Jacob, D.J., Cooper, O.R., et al., 2004. Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California. Journal of Geophysical Research 109 (D23), D23S10.

Hudman, R.C., Jacob, D.J., Turquety, S., et al., 2007. Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow. Journal of Geophysical Research 112, D12S05, doi:10.1029/2006JD007912.

Jacob, D.J., Logan, J.A., Murti, P.P., 1999. Effect of rising Asian emissions on surface ozone in the United States. Geophysical Research Letters, 26 (14), 2175–2178.

388 Jaffe D., Bertschi, I., Jaeglé, L., et al., 2004. Long-range transport of Siberian biomass
389 burning emissions and impact on surface ozone in western North America, Geophysical
390 Research Letters 31. L16106, doi:10.1029/2004GL020093.
391
392 Jaffe, D., Ray, J., 2007. Increase in surface ozone at rural sites in the western US.
393 Atmospheric Environment 41 (26) 5452–5463.
394
395 Jaffe, D., Chand, D., Hafner, W., Westerling, A., Spracklen, D., 2008, Influence of fires
396 on O_3 concentrations in the western US. Environmental Science and Technology 42 (16),
397 5885–5891.
398
399 Jaffe, D., 2011. Relationship between surface and free tropospheric ozone in the western
400 U.S.. Environmental Science and Technology 45, 432-438.
401
402 Liang, Q., Jaeglé, L., Hudman, R.C., et al., 2007. Summertime influence of Asian
403 pollution in the free troposphere over North America. Journal of Geophysical Research
404 112, D12S11, doi:10.1029/2006JD007919.
405
406 Kuhns, H., Knipping, E.M., Vukovich, J.M., 2005. Development of a United States-
407 Mexico emissions inventory for the Big Bend Regional Aerosol and Visibility
408 Observational (BRAVO) Study. Journal of the Air and Waste Management Association
409 55 (5), 677–692.
410
411 Langford, A.O., Aikin, K.C., Eubank, C.S., Williams, E.J., 2009. Stratospheric
412 contribution to high surface ozone in Colorado during springtime. Geophysical Research
413 Letters 36, L12801, doi:10.1029/2009GL038367.
414
415 Lefohn, A.S., Oltmans, S.J., Dann, T., Singh, H.B., 2001. Present-day variability of
416 background ozone in the lower troposphere. Journal of Geophysical Research 106 (D9),
417 9945–9958.
418
419 Li, Q., Jacob, D. J., Fairlie, T. D., et al., 2002. Stratospheric versus pollution influences
420 on ozone at Bermuda: Reconciling past analyses. Journal of Geophysical Research
421 107(D22), 4611, doi:10.1029/2002JD002138.
422
423 Li, Q.B., Jacob, D.J., Park, R., Wang, Y.X., Heald, C.L., Hudman, R., Yantosca, R.M.,
424 Martin, R.V., Evans, M., 2005. North American pollution outflow and the trapping
425 of convectively lifted pollution by upper-level anticyclone. Journal of Geophysical
426 Research 110 (D10), D10301.
427
428 Lin, C.-Y., Jacob, D.J., Munger, J.W., Fiore, A. M., 2000. Increasing background ozone
429 in surface air over the United States. Geophysical Research Letters 27 (21), 3465-3468.
430
431 Martin, R. V., Sauvage, B., Folkins, I., Sioris, C. E., Boone, C., Bernath, P., Ziemke, J.,
432 2007. Space-based constraints on the production of nitric oxide by lightning, Journal of
433 Geophysical Research 112, D09309, doi:10.1029/2006JD007831.

Mueller, S. F., Mallard, J. W., 2011. Contributions of natural emissions to ozone and PM2.5 as simulated by the Community Multiscale Air Quality (CMAQ) model. Environmental Science and Technology, accepted.

McLinden, C.A., Olsen, S. C., Hannegan, B., et al., 2000. Stratospheric ozone in 3-D models: a simple chemistry and the cross-tropopause flux, Journal of Geophysical Research, 105, 14653-14665, 2000.

Nowak, J. B., Parrish, D. D., Neuman, J. A., 2004. Gas-phase chemical characteristics of Asian emission plumes observed during ITCT 2K2 over the eastern North Pacific Ocean. Journal of Geophysical Research 109, D23S19, doi:10.1029/2003JD004488.

Olivier, J. G. J., Berdowski, J. J. M., 2001. Global emissions sources and sinks, in: Berdowski, J., et al. (Eds.), The Climate System, A.A. Balkema Publishers/Swets & Zeitlinger Publishers, Lisse, the Netherlands, pp. 33-78.

Oltmans, S. J., Lefohn, A. S., Harris, J. M., et al., 2010. Enhanced ozone over western North America from biomass burning in Eurasia during April 2008 as seen in surface and profile observations. Atmospheric Environment 44, 4497-4509.

Parrington, M., Jones, D.B.A., Bowman, K.W., et al., 2008. Estimating the summertime tropospheric ozone distribution over North America through assimilation of observations from the Tropospheric Emission Spectrometer. Journal of Geophysical Research 113, D18307, doi:10.1029/2007JD009341.

Parrington, M., Jones, D. B. A., Bowman, K. W., Thompson, A. M., et al., 2009. Impact of the assimilation of ozone from the Tropospheric Emission Spectrometer on surface ozone across North America. Geophysical Research Letters 36, L04802, doi:10.1029/ 2008GL036935.

Parrish, D. D., Millet, D. B., Goldstein, A. H., 2009. Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe. Atmospheric Chemistry and Physics 9, 1303–1323, doi:10.5194/acp-9-1303-2009.

Pickering, K. E., Wang, Y. S., Tao, W. K., Price, C., Muller J. F., 1998. Vertical distributions of lightning NOx for use in regional and global chemical transport models. Journal of Geophysical Research 103, 31,203– 31,216.

Price, C., Rind, D., 1992. A simple lightning parameterization for calculating global lightning distributions. Journal of Geophysical Research 97, 9919-9933.

Rastigejev, Y., Park, R., Brenner, M. P., Jacob, D. J., 2010. Resolving intercontinental pollution plumes in global models of atmospheric transport. Journal of Geophysical Research 115, D02302, doi:10.1029/2009JD012568.

480 Sauvage, B., Martin, R. V., van Donkelaar, A., Liu, X., Chance, K., Jaeglé, L., Palmer, P.
481 I., Wu, S., Fu, T.-M., 2007. Remote sensed and in situ constraints on processes affecting
482 tropical tropospheric ozone. Atmospheric Chemistry and Physics 7, 815– 838.
483
484 Singh, H.B., Anderson, B.E., Brune, W.H., et al., 2010. Pollution influences on
485 atmospheric composition and chemistry at high northern latitudes: Boreal and California
486 forest fire emissions. Atmospheric Environment 44, 4553-4564.
487
488 Thompson, A. M., Stone, J. B., Witte, J. C., et al., 2007. Intercontinental Chemical
489 Transport Experiment Ozonesonde Network Study (IONS) 2004: 2. Tropospheric ozone
490 budgets and variability over northeastern North America. Journal of Geophysical
491 Research 112, D12S13, doi:10.1029/2006JD007670.
492
493 US Environmental Protection Agency, 2006. Air Quality Criteria for Ozone and Related
494 Photochemical Oxidants (Final), Vols. I, II, and III. EPA 600/R-05/004aF-cF.
495
496 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, J. G., Kasibhatla, P., Arellano,
497 A. F., 2006. Interannual variability in global biomass burning emissions from 1997 to
498 2004. Atmospheric Chemistry and Physics 6, 3423-3441.
499
500 van Donkelaar, A., Martin, R.V., Leaitch, W.R. et al., 2008. Analysis of aircraft and
501 satellite measurements from the Intercontinental Chemical Transport Experiment
502 (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada. Atmospheric
503 Chemistry and Physics 8, 2999–3014.
504
505 Vestreng, V., Klein, H., 2002. Emission data reported to UNECE/EMEP. Quality
506 assurance and trend analysis and Presentation of WebDab, MSC-W Status Report 2002,
507 Norwegian Meteorological Institute, Oslo, Norway.
508
509 Walker, T. W., Martin, R. V., van Donkelaar, A., et al., 2010. Trans-Pacific transport of
510 reactive nitrogen and ozone to Canada during spring. Atmospheric Chemistry and
511 Physics 10, 8353-8372.
512
513 Wang, Y.H., Jacob, D.J., Logan, J.A., 1998. Global simulation of tropospheric O_3-NO_x-
514 hydrocarbon chemistry 3. Origin of tropospheric ozone and effects of nonmethane
515 hydrocarbons. Journal of Geophysical Research 103 (D9), 10757–10767.
516
517 Wang, Y.X., McElroy, M.B., Jacob, D.J., Yantosca, R.M., 2004. A nested grid
518 formulation for chemical transport over Asia: applications to CO. Journal of Geophysical
519 Research 109 (D22), D22307.
520
521 Wang, Y.X., Zhang, Y., Hao, J., Luo, M., 2011. Seasonal and spatial variability of
522 surface ozone over China: contributions from background and domestic pollution.
523 Atmospheric Chemistry and Physics 11, 3511–3525.
524

525 Wang, H., Jacob, D.J., Le Sager, P., Streets, D.G., Park, R.J., Gilliland, A.B., van
526 Donkelaar, A., 2009. Surface ozone background in the United States: Canadian and
527 Mexican pollution influences, Atmospheric Environment 43, 1310-1319.
528
529 Yienger, J. J., Levy II, H., 1995. Empirical model of global soil biogenic NOx emissions,
530 Journal of Geophysical Research 100, 11,447– 11,464.
531
532 Zhang, L., Jacob, D. J., Boersma, K. F., et al., 2008. Transpacific transport of ozone
533 pollution and the effect of recent Asian emission increases on air quality in North
534 America: an integrated analysis using satellite, aircraft, ozonesonde, and surface
535 observations. Atmospheric Chemistry and Physics 8, 6117-6136.
536
537 Zhang, L., Jacob, D. J., Kopacz, M., Henze, D. K., Singh, K., Jaffe, D. A., 2009.
538 Intercontinental source attribution of ozone pollution at western U.S. sites using an
539 adjoint method. Geophysical Research Letter 36, L11810, doi:10.1029/2009GL037950.
540
541 Zhang, L., Jacob, D.J., Liu, X., Logan, J.A., Chance, K., Eldering, A., Bojkov, B.R.,
542 2010. Intercomparison methods for satellite measurements of atmospheric composition:
543 Application to tropospheric ozone from TES and OMI. Atmospheric Chemistry and
544 Physics 10, 4725–4739.
545
546 Zhang, Q., Streets, D. G., Carmichael, G. R., et al., 2009. Asian emissions in 2006 for the
547 NASA INTEX-B mission. Atmospheric Chemistry and Physics 9, 5131-5153.
548
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Figure captions

Figure 1. CASTNet ozone monitoring sites in the continental United States for 2006. Sites in the intermountain West (Table 1) are indicated in red. Pluses denote sites above 1.5 km altitude.

Figure 2. March-August 2006 time series of daily 8-h max ozone concentrations at four representative sites in the US intermountain West. Model results (red line) are compared with observations (black line). Also shown is the North American background or PRB (blue line) and the natural background (green line). The mean concentrations for the time period and annual 4^{th}-highest ozone values (in parentheses) in ppbv are shown inset.

Figure 3. Simulated vs. observed daily 8-h max ozone concentrations for spring (March-May) and summer (June-August) 2006 at the 12 intermountain West CASTNet sites of Table 1. Also shown is the 1:1 line. The box-and-whisker plots (minimum, 25^{th}, 50^{th}, 75^{th} percentile, and maximum) give statistics of the North American background (PRB) and natural background for 10-ppbv bins of observed ozone concentrations.

Figure 4. Simulated (GEOS-Chem) vs. observed number of days with daily 8-h max ozone concentrations exceeding thresholds of 60, 65, and 70 ppbv in spring and summer 2006 at the 12 CASTNet sites in the intermountain West (Table 1). Symbols identify the individual sites.

Figure 5. Frequency distributions of daily 8-h max ozone concentrations in March-August 2006 for the ensemble of low-altitude (<1.5 km) and high-altitude CASTNet sites in the US (Figure 1). Model results (red) are compared to observations (black). Also shown are frequency distributions for the North American background (solid blue) and natural background (dashed green).

Figure 6. North American background (PRB) ozone concentration in surface air for spring and summer 2006. The top panels show seasonal means while the bottom panels show the means for days with ozone > 60 ppbv. Gray areas in the bottom panels had no days with ozone > 60 ppbv.

Figure 7. Annual 4^{th}-highest value of North American background ozone (PRB) calculated in GEOS-Chem as daily 8-h max and averaged for 2006-2008.

Table 1. Ozone concentrations at CASTNet monitoring sites in the US intermountain West [a]

Sites[b]	*r*	Spring		Summer		Annual 4th highest	
		Observed	GEOS-Chem (PRB)[c]	Observed	GEOS-Chem (PRB)	Observed	GEOS-Chem (PRB)
Yellowstone N.P., WY (44.6N, 110.4W, 2.4 km)	0.40	56.7	52.7 (40.8)	56.0	47.2 (35.3)	69.6	61.4 (51.3)
Pinedale, WY (42.9N, 109.8W, 2.4 km)	0.48	56.5	54.8 (41.9)	57.3	54.1 (38.6)	68.4	65.7 (53.5)
Centennial, WY (41.4N, 106.2W, 3.2 km)	0.20	59.5	54.9 (42.4)	56.1	56.1 (40.1)	70.4	66.6 (52.9)
Rocky Mountain NP, CO (40.3N, 105.6W, 2.8 km)	0.33	56.5	57.9 (44.6)	59.8	61.7 (39.4)	76.1	77.4 (55.3)
Gothic, CO (38.9N, 107.0W, 2.9 km)	0.21	58.8	56.0 (44.4)	53.9	55.4 (40.0)	70.0	65.3 (55.5)
Mesa Verde N.P., CO (37.2N, 108.5W, 2.2 km)	0.31	58.5	57.9 (44.4)	61.2	68.3 (45.6)	74.4	79.6 (58.1)
Great Basin N.P., NV (39.0N, 114.2W, 2.1 km)	0.52	54.5	52.8 (41.2)	58.9	59.2 (40.6)	72.2	72.6 (52.6)
Canyonlands N.P., UT (38.5N, 109.8W, 1.8 km)	0.36	56.6	56.3 (43.4)	59.7	60.3 (42.1)	70.6	70.9 (56.1)
Grand Canyon N.P., AZ (36.1N, 112.2W, 2.1 km)	0.38	58.8	56.6 (43.8)	58.8	60.6 (42.7)	70.8	69.9 (56.4)
Petrified Forest, AZ (34.8N, 109.9W, 1.7 km)	0.57	56.7	55.4 (42.5)	61.5	61.7 (43.3)	71.5	75.2 (57.9)
Chiricahua NM, AZ (32.0N, 109.4W, 1.6 km)	0.41	54.7	53.8 (43.1)	56.5	61.3 (45.1)	74.0	72.3 (58.9)
Big Bend NP, TX (29.3N, 103.2W, 1.1 km)	0.49	52.4	51.3 (39.3)	48.6	54.6 (40.8)	65.3	65.0 (52.3)

[a] Seasonal mean and annual 4th-highest daily 8-h max ozone values in ppbv for 2006 and correlation coefficients (*r*) between model and observations for the daily data. Spring is March-April and summer is June-August.

[b] NP = National Park, NM = National Monument, WY = Wyoming, CO = Colorado, NV = Nevada, UT = Utah, AZ = Arizona, TX = Texas.

[c] GEOS-Chem values in parentheses are the policy-relevant background ozone (PRB) as determined by a simulation with zero North American anthropogenic emissions.

Figures

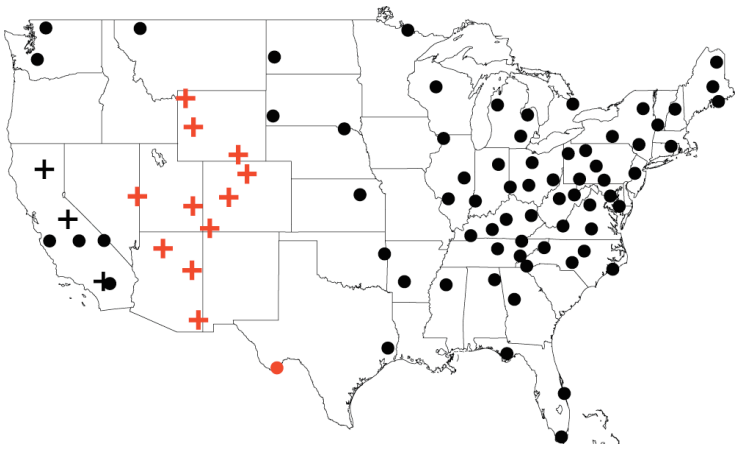


Figure 1. CASTNet ozone monitoring sites in the continental United States for 2006. Sites in the intermountain West (Table 1) are indicated in red. Pluses denote sites above 1.5 km altitude.

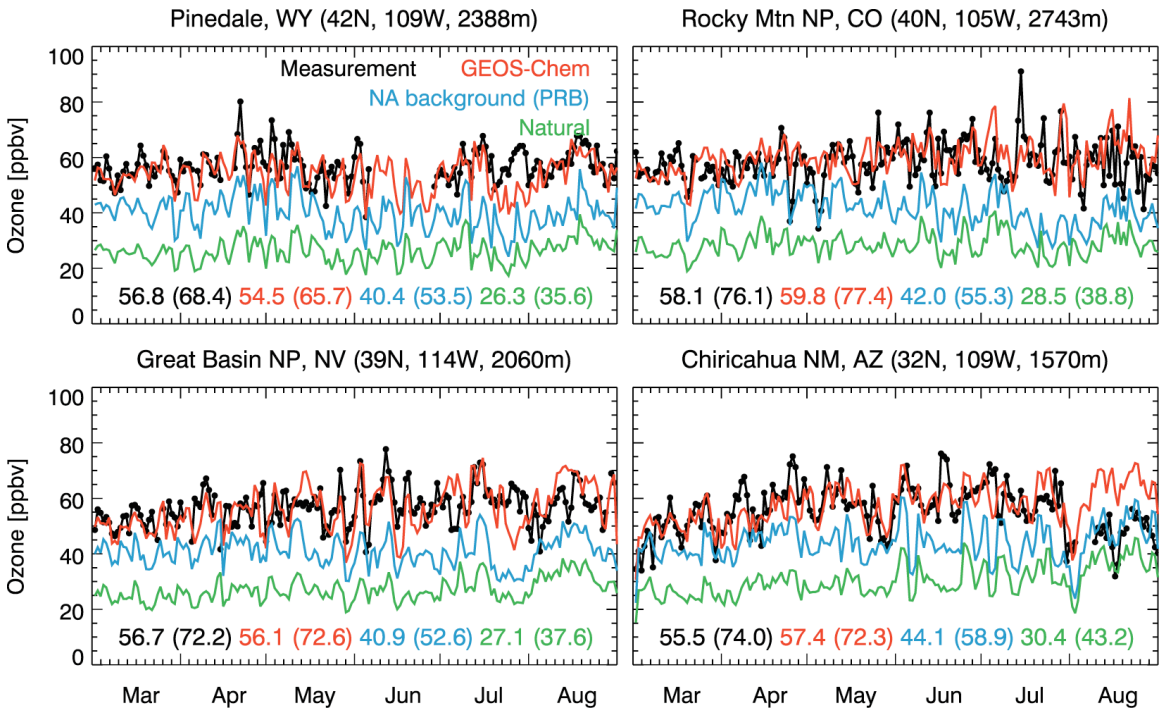


Figure 2. March-August 2006 time series of daily 8-h max ozone concentrations at four representative sites in the US intermountain West. Model results (red line) are compared with observations (black line). Also shown is the North American background or PRB (blue line) and the natural background (green line). The mean concentrations for the time period and annual 4th-highest ozone values (in parentheses) in ppbv are shown inset.

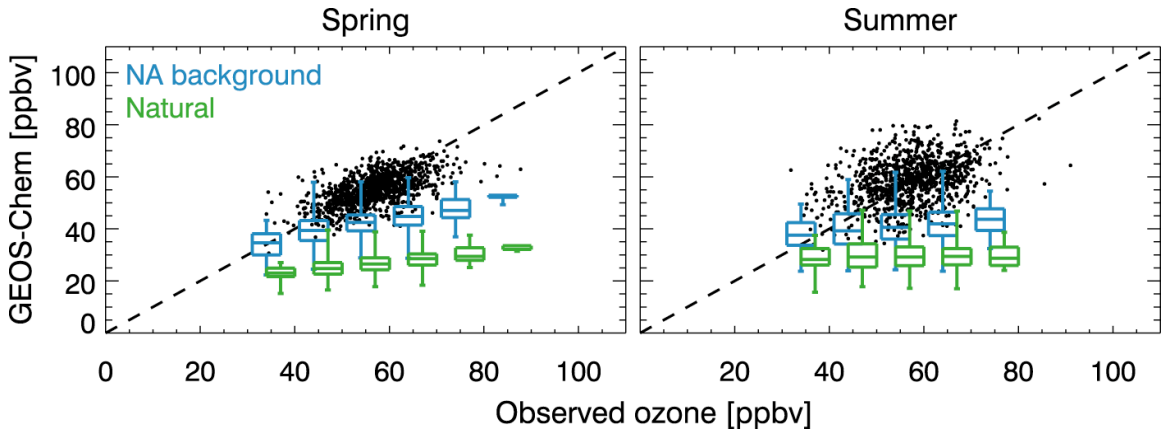


Figure 3. Simulated vs. observed daily 8-h max ozone concentrations for spring (March-May) and summer (June-August) 2006 at the 12 intermountain West CASTNet sites of Table 1. Also shown is the 1:1 line. The box-and-whisker plots (minimum, 25th, 50th, 75th percentile, and maximum) give statistics of the North American background (PRB) and natural background for 10-ppbv bins of observed ozone concentrations.

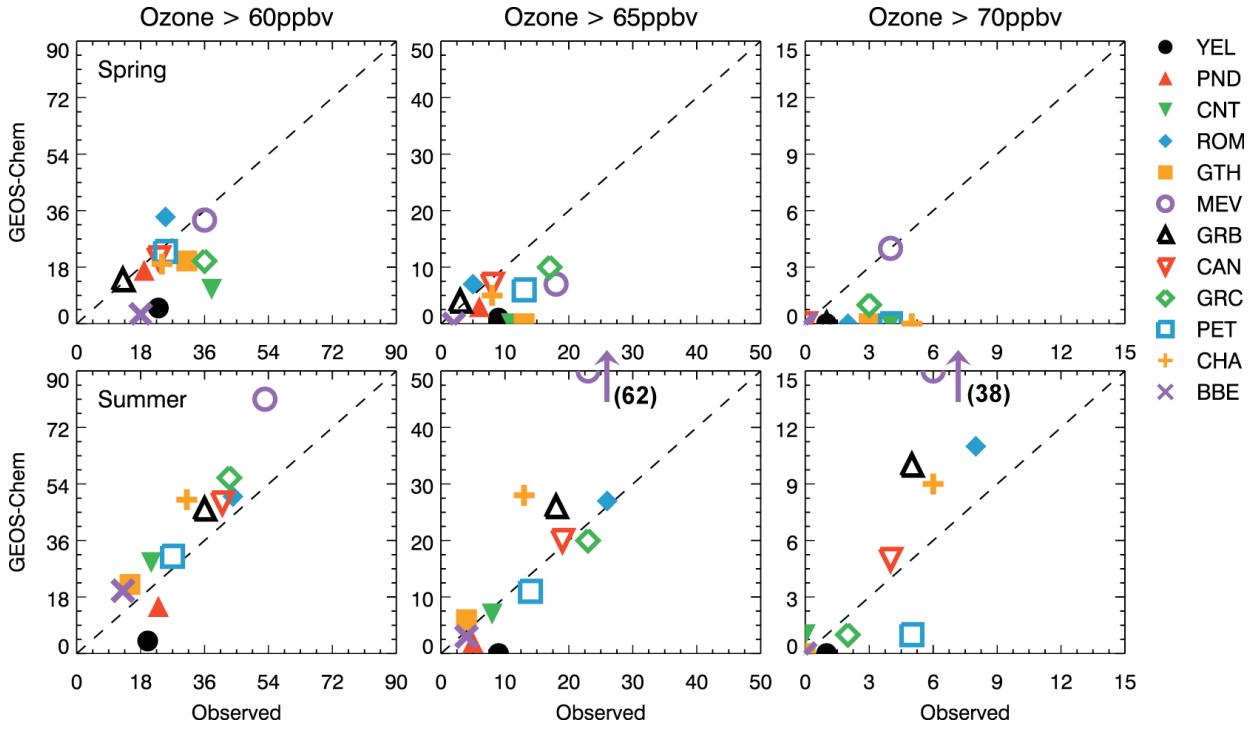
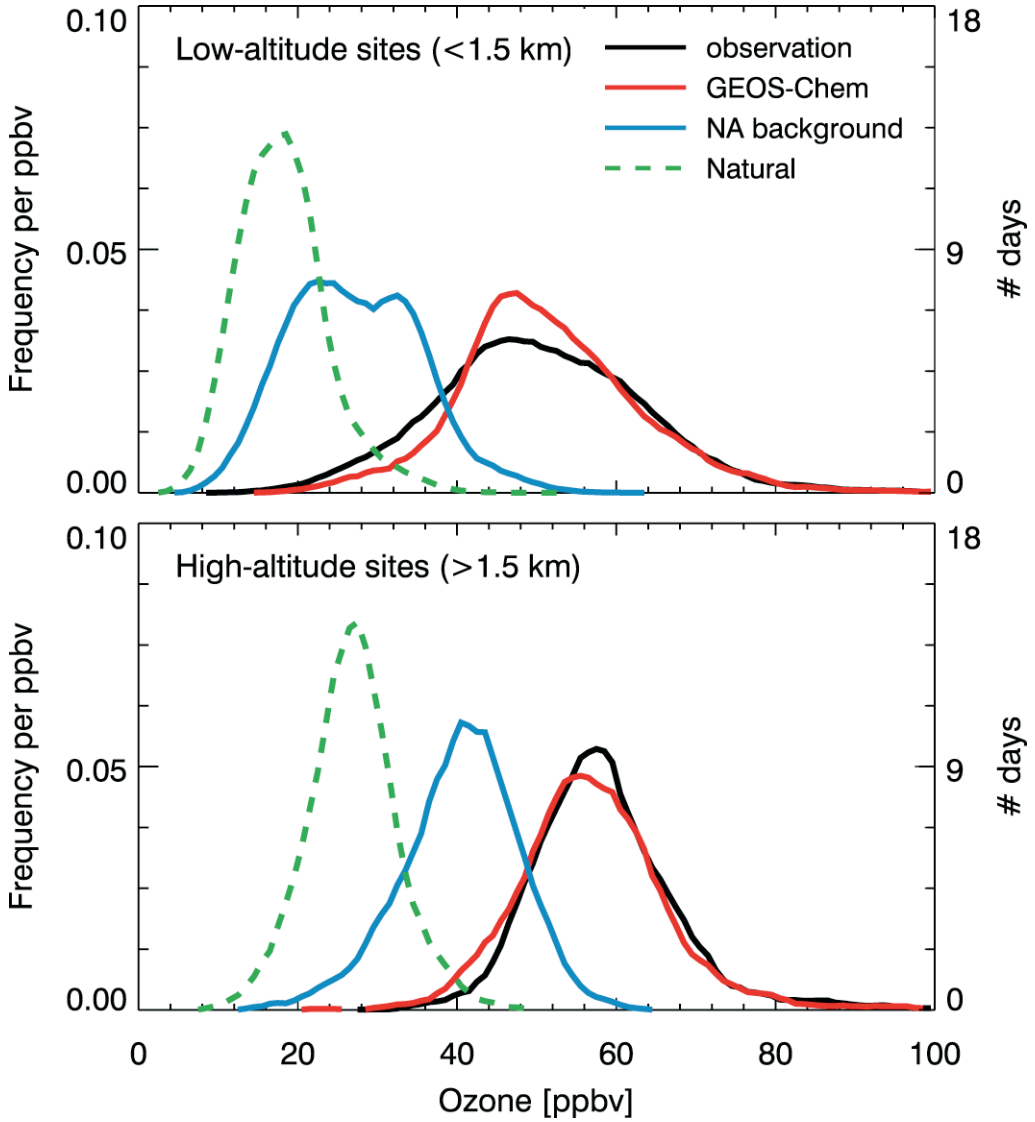


Figure 4. Simulated (GEOS-Chem) vs. observed number of days with daily 8-h max ozone concentrations exceeding thresholds of 60, 65, and 70 ppbv in spring and summer 2006 at the 12 CASTNet sites in the intermountain West (Table 1). Symbols identify the individual sites.



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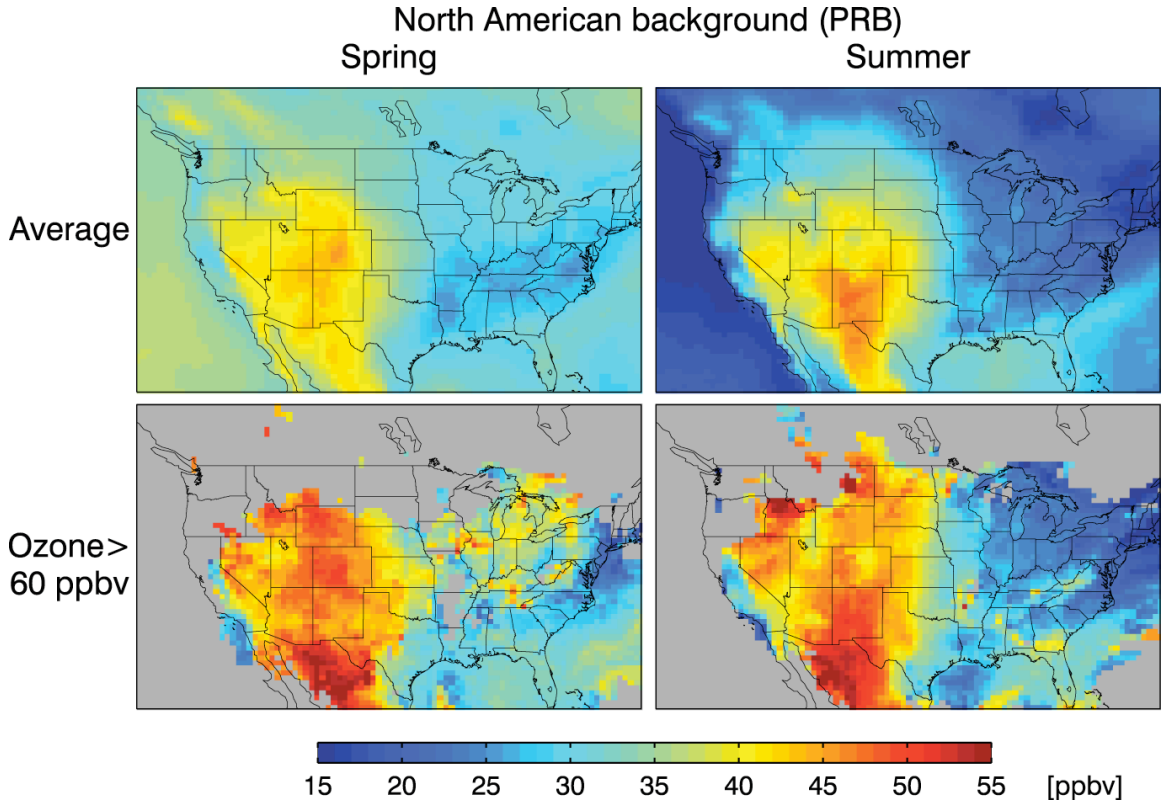

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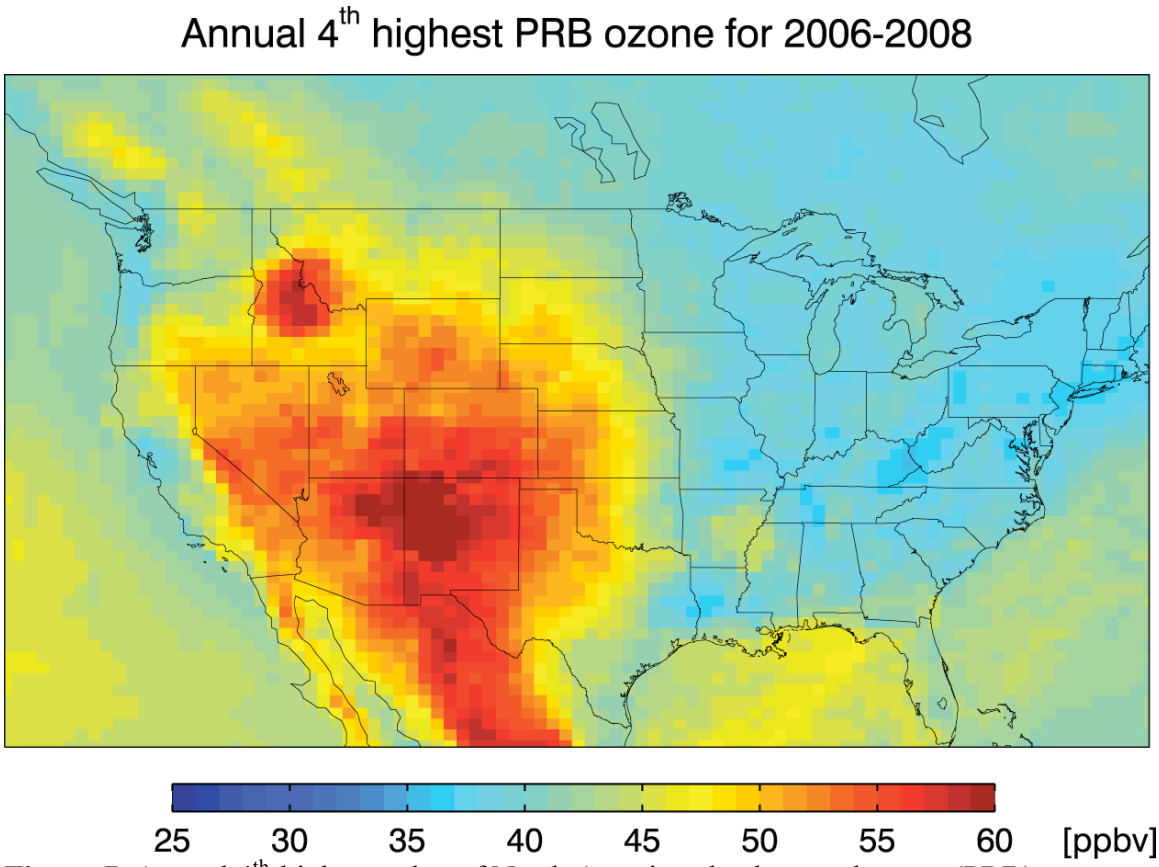

Figure 7. Annual 4th-highest value of North American background ozone (PRB) calculated in GEOS-Chem as daily 8-h max and averaged for 2006-2008.

Supplemental Material

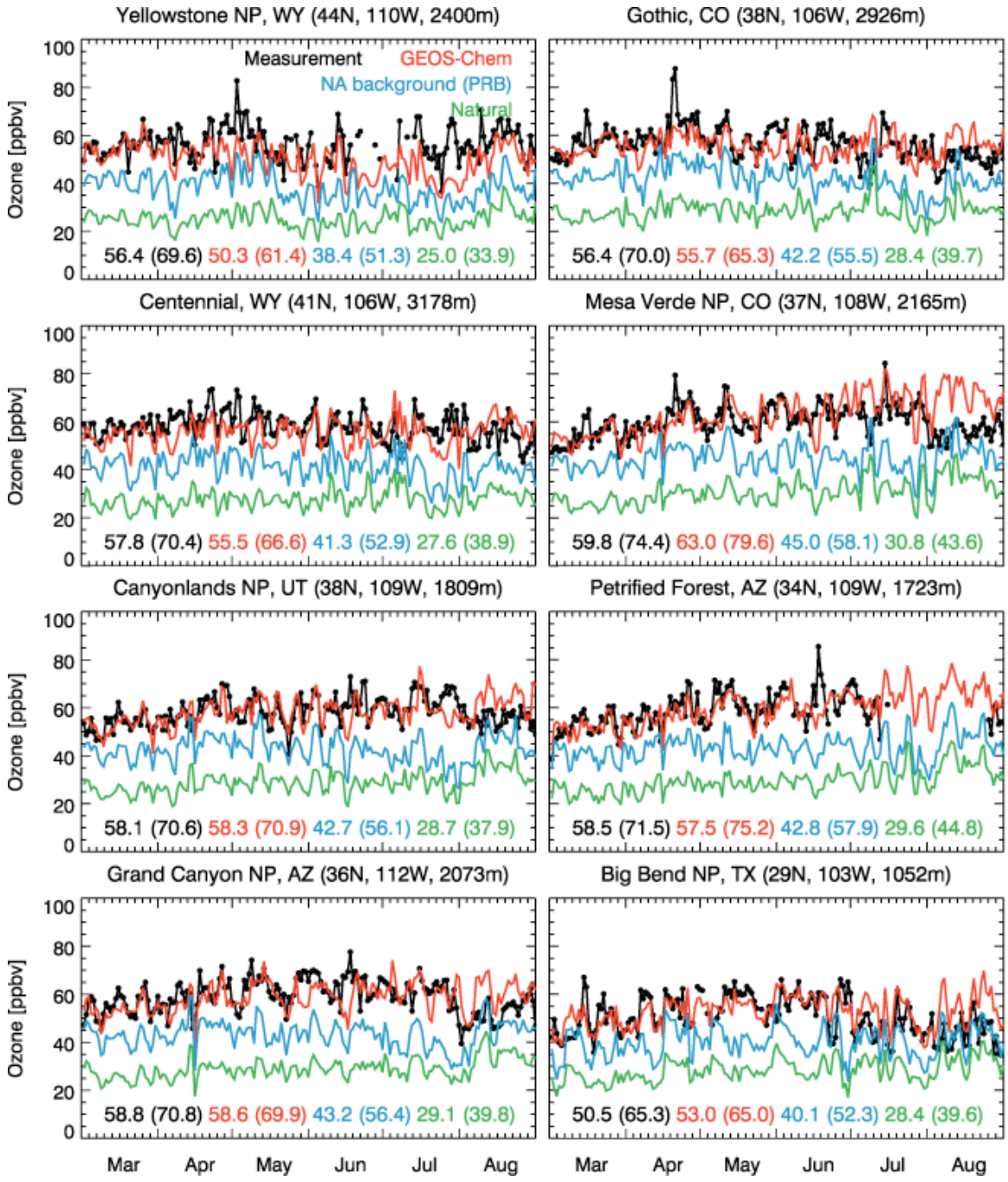

Figure S1. March-August 2006 time series of daily 8-h max ozone concentrations at the additional intermountain West sites of Table 1. Model results (red line) are compared with observations (black line). Also shown is the North American background or PRB (blue line) and the natural background (green line). The mean concentrations for the time period and annual 4th-highest ozone values (in parentheses) in ppbv are shown inset.

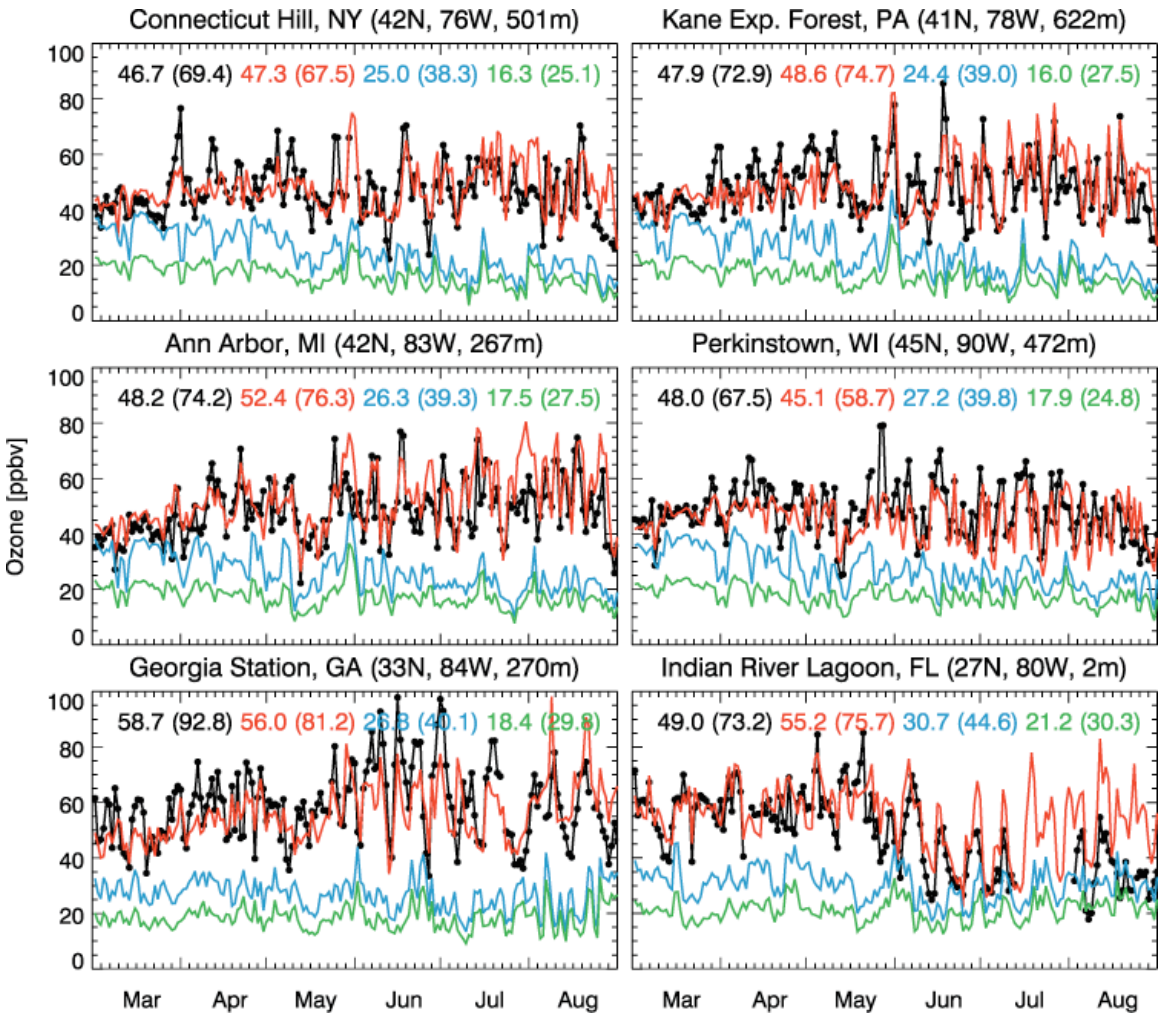

Figure S2. The same as Figure S1, but for representative CASTNet sites in the Northeast US (top), Great Lakes (middle), and the Southeast US (bottom).

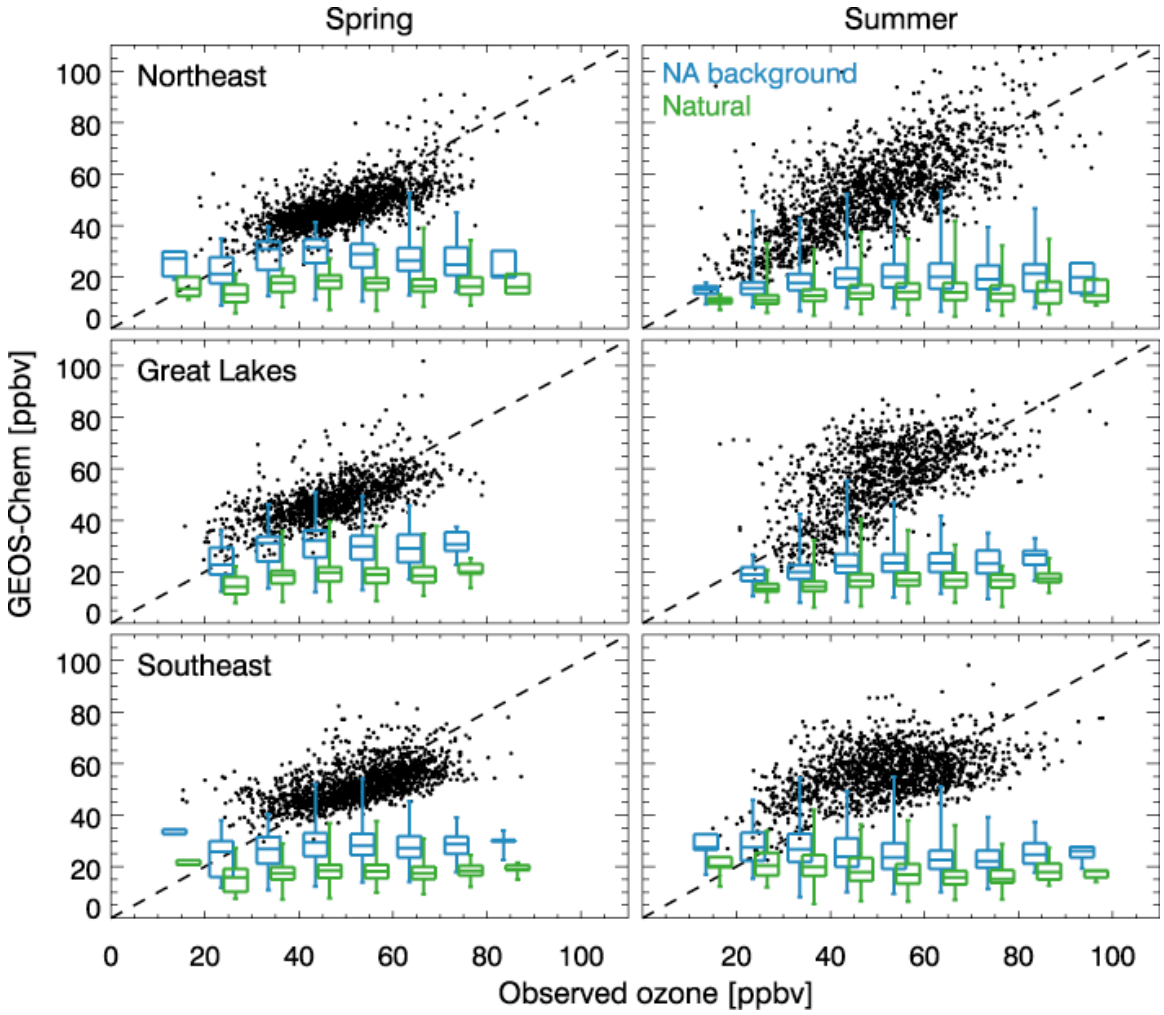

Figure S3. Simulated vs. observed daily 8-h max ozone concentrations for spring (March-May) and summer (June-August) 2006 for the ensembles of CASTNet sites in the Northeast US, Great Lakes, and the Southeast US. Also shown is the 1:1 line and North American background (PRB) and natural background model statistics for 10-ppbv bins of observed ozone concentrations: the minimum, 25th, 50th, 75th percentile, and maximum.